

SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 03076114.2 filed 15 April 2003.--

Paragraph on line 1 of page 1 has been amended as follows:

-- The invention ~~is directed~~ relates to a process for the preparation of hydrogen and a mixture of hydrogen and carbon monoxide.--

Paragraph on line 3 of page 2 has been amended as follows:

-- ~~US-A-Pat. No.6224789~~ discloses a process wherein synthesis gas is prepared in a combination of an autothermal steam reforming step and a convective steam reforming step.

Paragraph on line 10 of page 2 has been amended as follows:

-- The synthesis gas as obtained in the above processes may be used as feedstock in a Fischer-Tropsch process. In typical Fischer-Tropsch processes hydroprocessing steps are performed to covert the Fischer-Tropsch synthesis paraffinic product into valuable products as detergent feedstock, solvents, naphtha, kerosene, gas oil, lubricating base oils and waxes having varying congealing points. Typical hydroprocessing steps are hydrogenation, ~~hydroisomerisation~~ hydroisomerization, hydrocracking and catalytic dewaxing. For these steps hydrogen is needed. ~~The object of the present invention is~~ It would be useful to provide an efficient process to simultaneously prepare hydrogen and synthesis gas.--

Paragraph on line 23 of page 2, ending on line 5 of page 3 has been amended as follows:

-- The invention provides a process ~~Process~~ for the preparation of hydrogen and a mixture of hydrogen and carbon monoxide containing gas from a carbonaceous feedstock by performing the following steps:

(a) preparing a mixture of hydrogen and carbon monoxide having a temperature of above 700 °C

- (b) ~~catalytic~~ catalytically steam reforming a carbonaceous feedstock in a Convective Steam Reformer zone, wherein the required heat for the steam reforming reaction is provided by convective heat exchange between the steam reformer reactor zone and the effluent of step (a) to obtain as separate products a steam reforming product having a hydrogen to ~~CO~~ carbon monoxide molar ratio of greater than 2 and a cooled effluent of step (a), and
- (c) separating hydrogen from the steam reforming product.

~~Applicants have found that the process according to the invention can prepare a synthesis gas useful in a Fischer-Tropsch process and simultaneously prepare hydrogen useful in the downstream hydroprocessing units. The invention further provides the additional steps of:~~

- (d) catalytically converting the hydrogen and carbon monoxide into a stream comprising hydrocarbons via a Fischer-Tropsch process, and
- (e) separating the stream of step(d) into a hydrocarbon product and a gaseous recycle stream
- and also optionally
- (f) hydroprocessing the hydrocarbon product of step (e) with the hydrogen from step (c).--

Paragraph on line 31 of page 3, ending on line 11 of page 4 has been amended as follows:

-- A preferred embodiment for step (a) is the well known autothermal reformer (ATR) process. The feedstock of the ATR autothermal reformer may be a hydrocarbon containing feedstock such as natural gas. Preferably part of the steam reformer product as prepared in step (b) is used as feed in step (a) wherein it is partially oxidized with an oxygen containing gas in the ATR autothermal reformer. Such an ATR autothermal reformer step may be performed in a conventional type ATR autothermal reformer reactor consisting of a refractory lined, possibly water jacketed, vessel, to which the feed is supplied to a suitable burner nozzle. The products of the resulting flame reaction are brought towards equilibrium over a nickel secondary reforming catalyst as present in the catalyst bed in the lower part of such a ATR an autothermal reformer reactor vessel.--

Paragraph on line 12 of page 4 has been amended as follows:

--Another preferred embodiment for step (a) is the non-catalyzed partial oxidation (~~POX~~) partial oxidation of the carbonaceous feedstock and oxygen. An advantage of

performing a partial oxidation or a ~~ATR~~ an autothermal reformer in step (a) is that the H_2/CO hydrogen to carbon monoxide molar ratio's ratios of the combined synthesis gas products of step (a) and partly in step (b) can be from 1.5 up to 3 and even preferably from 1.9 up to 2.3, making the synthesis gas product suitable for various applications as will be discussed here below.--

Paragraph on line 21 of page 4 has been amended as follows:

-- The carbonaceous feedstock in the partial oxidation and in step (b) is preferably a gaseous hydrocarbon, suitably methane. In the context of the present invention, a methane feedstock includes natural gas, associated gas or a mixture of C_{1-4} hydrocarbons. The gaseous ~~hydrocarbons~~ hydrocarbon suitably comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C_{1-4} hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Preferably natural gas or associated gas is used. Preferably any ~~sulphur~~ sulfur in the feedstock is removed prior to using said gas as feedstock in step (b) and optionally in step (a).--

Paragraph on line 3 of page 5 has been amended as follows:

-- Preferably, the feed in the partial oxidation or in the conventional steam reforming processes for step (a) and for step (b) is a gaseous feed as described above. In such a preferred embodiment from 10 wt% to 90 wt%, more preferably from 20 wt% to 50 wt%, of the total gaseous feed to steps (a) and (b) is fed to step (b). --

Paragraph on line 9 of page 5 has been amended as follows:

-- In step (a) the partial oxidation may be performed according to well known principles as, for example, described for the Shell Gasification Process in the Oil and Gas Journal, September 6, 1971, pp 85-90. Publications describing examples of partial oxidation processes are EP-A-291111, WO-A-9722547, WO-A-9639354 and WO-A-9603345. In such processes the feed is contacted with an oxygen containing gas under partial oxidation conditions preferably in the absence of a catalyst.--

Paragraph on line 27 of page 5, ending on line 4 of page 6 has been amended as follows:

-- Contacting the feed in a ~~POX~~ partial oxidation process step with the oxygen containing gas in step (a) is preferably performed in a burner placed in a reactor vessel. To adjust the H_2/CO hydrogen to carbon monoxide ratio in the gaseous product obtained in the partial oxidation reaction in step (a), carbon dioxide and/or steam may be introduced into the feed. Preferably up to 15% volume based on the amount of gaseous product, preferably up to 8% volume, more preferably up to 4% volume, of either carbon dioxide or steam is added to the feed. As a suitable steam source, water produced in an optional downstream hydrocarbon synthesis may be used.--

Paragraph on line 5 of page 6 has been amended as follows:

--The gaseous product of the partial oxidation reaction in step (a) preferably has a temperature of between 1100 °C and 1500 °C and ~~an H_2/CO~~ a hydrogen to carbon monoxide molar ratio of from 1.5 up to 2.6, preferably from 1.6 up to 2.2.--

Paragraph on line 9 of page 6 has been amended as follows:

-- Step (b) may be performed by well-known steam reforming processes, wherein steam and the gaseous hydrocarbon feed are contacted with a suitable reforming catalyst in a ~~CSR~~ convective steam reformer reactor. The convective steam reactor zone preferably comprises of a tubular reactor vessel provided with one or more tubes containing a reforming catalyst. Various designs for such a reactor are known and suited for the present invention. Examples of such reactors are described in WO-A-0137982, EP-A-983964 or WO-A-8801983.--

Paragraph on line 19 of page 6, ending on line 15 of page 7 has been amended as follows:

-- The catalyst and process conditions as applied in the convective steam reformer zone may be those known by the skilled person in the field of steam reforming. Suitable catalysts comprise nickel optionally applied on a carrier, ~~for example,~~ for example, alumina. The space velocity of the gaseous feed is preferably from 700 liter to 1000 ~~litre~~ liter (S.T.P.)/~~litre~~ liter catalyst/hour, wherein S.T.P. means Standard Temperature of 15 °C and pressure of 1 bar abs. The steam to carbon (as hydrocarbon and ~~CO~~ carbon monoxide) molar ratio is preferably from 0 up to 2.5 and more preferably below 1 and most preferably from 0.5 up to 0.9. If such low steam to carbon ~~ratio's~~ ratios are applied in step (b) the catalyst preferably comprises a Group VIII metal. More preferably the catalyst comprises (a) an oxidic support material and (b) a coating comprising between about 0.1 and about

7.0 wt% of at least one of the metals ~~of~~ selected from the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising: (i) at least 80 wt% of ZrO_2 which has been calcined at a temperature up to about 670 °C before the application of said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of oxides of Y, La, Al, Ca, Ce and Si, preferably La_2O_3 . Examples of such catalysts include are, for example, the catalyst described in EP-A-695279. Preferably, the feed also comprises an amount of CO_2 carbon dioxide, wherein preferably the CO_2 carbon dioxide ~~over to~~ carbon (as hydrocarbon and CO carbon monoxide) molar ratio is from 0.5 up to 2. The product gas of step (b) preferably has a temperature of from 600 °C up to 1000 °C and a hydrogen to carbon monoxide ~~an H_2/CO~~ molar ratio of from 0.5 up to 2.5.--

Paragraph on line 16 of page 7 has been amended as follows:

-- The temperature of the hydrogen and carbon monoxide containing gas of step (a) is preferably reduced in step (b) from a temperature of from 1000 °C up to 1500 °C to a temperature from 300 °C up to 750 °C. The temperature of the metal wall surfaces of the reactor tubes in the convective steam reformer zone in step (b) is preferably maintained below 1100 °C.--

Paragraph on line 23 of page 7 has been amended as follows:

-- The mixture of carbon monoxide and hydrogen (steam reformer product) may be used exclusively to prepare hydrogen or may partly also be combined with the product gas as obtained in step (a), provided to the partial oxidation reactor of step (a) or used as feedstock in case an ATR autothermal reformer is used in step (a) as explained above. Suitably more than 10 vol% of the steam reformer product as obtained in step (b) is used in step (c).--

Paragraph on line 31 of page 7, ending on line 25 of page 8 has been amended as follows:

-- In a preferred embodiment, part of the steam reforming product as obtained in step (b) is fed to step (a) in case step (a) is a ~~POX~~ partial oxidation process step. The invention is also directed to encompass below process embodiments wherein a convective steam reactor is used which has separate outlets for the steam reactor product and the cooled effluent of step (a). An advantage of mixing part of the steam reformer product of step (b)

with the feed to step (a) or more preferably directly into the partial oxidation reactor of step (a) is that any methane or higher gaseous hydrocarbon, which may still be present in the steam reformer product, is then further converted to hydrogen and carbon monoxide. This is especially advantageous when the steam reforming step (b) is performed on a feed having a steam to carbon ratio of less than 1, especially between 0.5 and 0.9. Operating the process with a lower steam to carbon ratio in the feed to step (b) is advantageous because the resulting synthesis gas product will then also contain less steam and because smaller reactor equipment may be applied. ~~A disadvantage of~~ However, by operating step (b) at a low steam to carbon ratio ~~is that~~ more unconverted methane will be present in the steam reformer product. ~~By~~ This is resolved by routing part of the steam reformer product to step (a) ~~this disadvantage is overcome~~. The combined mixture is used in step (b) to provide the required reaction heat for performing step (b).--

Paragraph on line 3 of page 9 has been amended as follows:

-- Preferably, the steam reformer product (55) is fed close, i.e. in the upper half of vessel (51), to the burner (52) in order to benefit the most of from the resultant elevated temperatures of from 800 °C up to 1050 °C present in that region of the vessel (51) enabling conversion of methane which may be present in product (55). The methane content in steam reformer product (55) may be between 5 mol% and 30 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b), (43). This relatively high methane content results is a resultant when operating step (b) at relatively lower temperatures and/or at relatively low steam to carbon ratio as described before. Low temperatures in step (b) are suitably between 700 °C and 800 °C as measured on steam reformer product (55) as it leaves the reactor (44). A low temperature is desirable for material strength reasons for the internals used in reactor (44).--

Paragraph on line 20 of page 9, ending on line 5 of page 10 has been amended as follows:

--Another embodiment which aims at operating step (b) such that the temperature of the reactor (44) internals is kept at acceptable levels is by allowing on the one hand a higher outlet temperature for steam reformer product (55) and on the other hand reducing the temperature of (56). This is achieved by mixing steam reformer product, shown as dotted line (55'), with the gaseous product of the partial oxidation reaction at a position spaced away from the burner (52), such that no significant conversion of methane present in steam reformer

product (55') will take place when mixing these two streams. Preferably mixing is performed in the lower part of reactor vessel (51). Due to mixing of the product of the partial oxidation reaction having a temperature of between 1100 °C and 1500 °C and steam reformer product (55) having a considerable lower temperature, a temperature reduction relative to the temperature of the product of the partial oxidation reaction of between 250 °C and 500 °C will result.--

Paragraph on line 6 of page 10 has been amended as follows:

-- Because the outlet temperature of steam reformer product (55') is suitably higher than in the above described embodiment stream steam reformer product (55') will have a relatively lower methane content, suitably between 1 mol% and 10 mol% carbon and preferably between 2 mol% and 5 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b), (43). --

Paragraph on line 13 of page 10 has been amended as follows:

-- This methane is preferably converted in a preferred autothermal reformer step (g), also referred to as catalytic post reforming, as present in the lower half of reactor vessel (51). The post reforming catalyst bed (53) may be any well-known reformer catalyst, for example, a Ni-containing catalyst or any catalyst described above for the ~~CSR~~ convective steam reforming reactor. The effluent of the autothermal reformer step (g) is subsequently fed to inlet (38) of convective steam reforming reactor vessel (44), wherein the gasses supply heat to the convective steam reforming zone. The final synthesis gas product (63) is obtained via outlet (42).--

Paragraph on line 25 of page 10 has been amended as follows:

-- In step (g) a temperature reduction is achieved of suitably between 20 °C and 70 °C and preferably between 40 °C and 60 °C. Stream (56) as obtained in step (g) and having a reduced methane content preferably has a temperature of between 950 °C and 1100 °C and more preferably a temperature between 980 °C and 1050 °C. The methane conversion in step (g) is suitably between 10 wt% and 50 wt%.--

Paragraph on line 32 of page 10, ending on line 5 of page 11 has been amended as follows:

-- Also shown in Figure 1 is how part (60) of the steam reformer product (55) having a relatively high hydrogen over CO carbon monoxide molar ratio is separated from steam reformer product (55). In Figure 2 is shown how this stream (60) is fed according to step (c) to a hydrogen recovery unit (61) to obtain hydrogen (62) ~~suitably~~ suitable for use in hydroprocessing unit(s) (66). --

Paragraph on line 6 of page 11 has been amended as follows:

-- The molar hydrogen to CO carbon monoxide ratio in steam reformer product (60) is higher than 2, preferably higher than 3 and typically not greater than 6. The hydrogen recovery unit (61) may be well known membrane separation units, pressure swing absorbers (PSA) or combinations of a membrane unit followed by a PSA pressure swing absorber.--

Paragraph on line 12 of page 11 has been amended as follows:

-- The synthesis gas (63) as obtained by the above process may advantageously be used as feedstock for a Fischer-Tropsch synthesis process, methanol synthesis process, a dimethyl ether synthesis process, an acetic acid synthesis process, ammonia synthesis process or to other processes which use a synthesis gas mixture as feed, ~~such as~~ for example, processes involving carbonylation and hydroformylation reactions. To steps (a) and (b) preferably recycle gases are fed. These recycle gases are obtained in, for example, the above exemplified, processes which use the synthesis gas as prepared by the process according to the invention. These recycle gases may comprise C_{1-5} hydrocarbons, preferably C_{1-4} hydrocarbons, more preferably C_{1-3} hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethylether, or acetic acid may be present. --

Paragraph on line 30 of page 11, ending on line 13 of page 12 has been amended as follows:

-- The invention is especially directed to the above process for the preparation of hydrogen and carbon monoxide containing gas (synthesis gas), wherein additional steps (d) (e) and (f) are also performed. In step (d) the synthesis gas is catalytically converted using a

Fischer-Tropsch catalyst into a hydrocarbons comprising stream. In step (e) the hydrocarbons comprising stream of step (d) is separated into a hydrocarbon product and a gaseous recycle stream. Suitably the hydrocarbon product ~~are these~~ comprises hydrocarbons having 5 or more carbon atoms, preferably having 4 or more carbon atoms and more preferably having 3 or more carbon atoms. The gaseous recycle stream may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water.--

Paragraph on line 22 of page 12 has been amended as follows:

-- Step (d) and (e) may be performed by the well known Fischer-Tropsch processes which are for example the Sasol process and the Shell Middle Distillate Process. Examples of suitable catalysts are based on iron and cobalt. Typical reactor configurations include slurry reactors and tubular reactors. These and other processes are, for example, described in more detail in EP-A-776959, EP-A-668342, ~~US-A-4943672~~ US Pat. No. 4943672, ~~US-A-5059299~~ US Pat No. 5059299, WO-A-9934917 and WO-A-9920720, all of which are herein incorporated by reference.--

Paragraph on line 31 of page 12, ending on line 6 of page 13 has been amended as follows:

-- Figure 2 illustrates the configuration of Figure 1 in combination with a Fischer-Tropsch synthesis process unit (64) and its downstream hydroconversion unit(s) (66). In addition to Figure 1, Figure 2 shows how the synthesis gas (63) is fed to Fischer-Tropsch synthesis process unit (64). In unit (64) a gaseous recycle stream (54) is separated from the hydrocarbon product (65) and recycled to the partial oxidation reactor (51).--

Paragraph on line 7 of page 13 has been amended as follows:

In the hydroprocessing units, the hydrocarbon product present in (65), comprising typically a relatively large portion of compounds boiling above 370 °C, is converted by well-known hydrocracking and ~~hydroisomerisation~~ hydroisomerization processes to middle distillates, for example, such as kerosene and or gas oil products. Any remaining residue may be further converted to base oils by catalytic dewaxing processes (not shown), which also require hydrogen. Examples of such downstream hydroprocessing units are described in for example WO-A-0107538, WO-02070631, WO-02070629 and WO-02070627, all of which are herein incorporated by reference, and in the references cited in these publications.--

Paragraph on line 19 of page 13 has been amended as follows:

– The hydroprocessing unit (66) may also be ~~[[e]]~~ a hydrogenation unit in which ~~selectively~~ the oxygenates and olefins as present in a Fischer-Tropsch synthesis product (65) are selectively converted, in the presence of hydrogen and a suitable hydrogenation catalyst, to paraffins in order to obtain a variation of products comprising substantially ~~of~~ normal paraffins. Examples of these products are solvents boiling in the naphtha to kerosene range, linear detergent feedstocks having carbon numbers between 109 and 19 and waxes having congealing points between 30 °C and 150 °C.--